BS EN 1988-1:1998

Foodstuffs — Determination of sulfite —

Part 1: Optimized Monier-Williams method

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ICS 67.040

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— present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

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Summary of pages

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Foreword

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This European Standard: *Foodstuffs — Determination of sulfite* consists of the following parts:

Part 1: Optimized Monier-Williams method;
Part 2: Enzymatic method.

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Introduction

Sulfite can be used as a preservative of foodstuffs. In order to minimize possible negative health effects, many countries have regulated the use of sulfite in foods. This has resulted in the development of several methods of analysis to detect the presence and quantity of sulfite in a great variety of foods.

1 Scope

This European Standard specifies a distillation method for the determination of the sulfite content, expressed as sulfur dioxide, in foodstuffs, in which the content of sulfite is at least 10 mg/kg. The method is applicable in the presence of other volatile sulfur compounds. It is not applicable to cabbage, dried garlic, dried onions, ginger, leeks and soy proteins[1)]. It has been shown that the analysis of isolated soy protein leads to false positive results.

Specific products, for which European Standards for the determination of the sulfites exist, are excluded from the scope of this horizontal European Standard.

2 Normative references

This part of this European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods* (ISO 3696:1987).

3 Principle

Free sulfite plus reproducible portion of bound sulfites (such as carbonyl addition products) in foods are measured. The test portion is heated with a refluxing solution of hydrochloric acid to convert sulfite to sulfur dioxide. A stream of nitrogen is introduced below the surface of the refluxing solution to sweep sulfur dioxide through a water-cooled condenser and, via a bubbler attached to the condenser, into the hydrogen peroxide solution, where sulfur dioxide is oxidized to sulfuric acid. The generated sulfuric acid is titrated with standardized sodium hydroxide solution. The sulfite content is directly related to the generated sulfuric acid. See [1], [2].

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only water of at least grade 3 as defined in EN ISO 3696.

4.1 *Hydrochloric acid*, substance concentration $c(HCl)$ = 4 mol/l.

For each analysis, prepare 90 ml of solution by adding (carefully) 30 ml of concentrated hydrochloric acid (36 %) to 60 ml of water and mix. Prepare a fresh solution daily.

4.2 *Sodium hydroxide standard solution*, $c(NaOH)$ = 0,010 mol/l.

4.3 *Methyl red indicator*.

Dissolve 250 mg of methyl red in 100 ml of ethanol.

4.4 *Hydrogen peroxide solution*, volume fraction $\varphi (H_2O_2)$ = 3 %.

Just prior to use, add 3 drops of methyl red indicator and titrate with sodium hydroxide standard solution (**4.2**) to yellow end point. If end point is exceeded, discard the solution.

4.5 *Ethanol* or *methylated spirit*.

4.6 *Ethanol–water mixture*, volume fraction φ of ethanol = 5 %.

4.7 *Nitrogen*.

High purity, used with regulator to maintain flow of 200 ml/min.

To guard against oxygen in nitrogen gas, use an absorber as used in the gas chromatographic analysis.

Alternatively, an oxygen-scrubbing solution, such as alkaline 1,2,3 trihydroxibenzene (pyrogallol), in a gas-washing bottle may be used. Prepare the gas-washing bottle as follows. Add 4,5 g of 1,2,3 trihydroxibenzene to the gas-washing bottle. Purge the gas-washing bottle with nitrogen for 2 min to 3 min. Prepare a potassium hydroxide solution by adding 65 g of potassium hydroxide to 85 ml of water. (Caution: heat is generated). Add the potassium hydroxide solution to the gas-washing bottle while an atmosphere of nitrogen is maintained in the gas-washing bottle.

[1)] It has been shown that the analysis of isolated soy protein leads to false positive results in the range of 20 mg/kg to 30 mg/kg expressed as sulfur dioxide. Therefore, when analysing foodstuffs containing isolated soy proteins a proportional enhancement of the result may be obtained and is taken into account.

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5 Apparatus

5.1 *Distillation apparatus.*

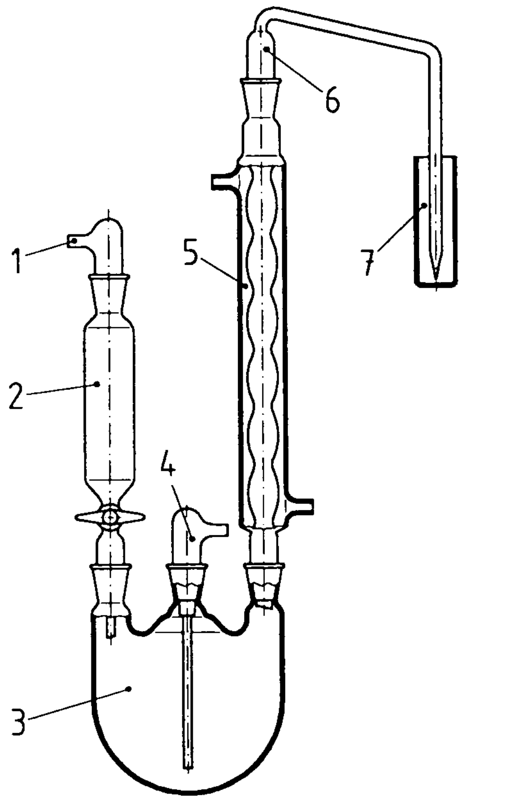
Assemble the apparatus[2)] (see Figure 1), which includes the following.

— Inlet adapter (1) with hose connector and rubber bulb to apply a head pressure above the solution. The use of a pressure equalizing dropping funnel is not recommended because the condensate, possibly containing sulfur dioxide, is deposited in the funnel and side arm.

— Cylindrical dropping funnel (2) of ≥ 100 ml capacity.

— Round-bottomed flask (3) of capacity 1 l, with three suitable leakproof joints.

— Gas inlet tube (4) of sufficient length to permit the introduction of nitrogen within 25 mm of the bottom of the flask.



1 Inlet adapter
2 Cylindrical dropping funnel
3 Round-bottomed flask
4 Gas inlet tube
5 Bulb condenser
6 Bubbler
7 Vessel

Figure 1 — Distillation apparatus for optimized Monier-Williams method

— Bulb condenser (5), jacket length 300 mm.

— Bubbler (6), fabricated from glass according to dimensions in Figure 2.

— Vessel (7), of approximately 25 mm inner diameter and 180 mm length.

NOTE If back pressure is kept as low as possible, losses of sulfur dioxide through leaks can be avoided. A thin film of stopcock grease on sealing surfaces of all joints except the joint between the cylindrical dropping funnel and the flask is helpful. Joints which are clamped together help to ensure a complete seal throughout the analysis.

5.2 *Burette*, of capacity 10 ml with overflow tube and hose connections for sodium hydroxide adsorbed on silicon dioxide, or an equivalent air-scrubbing apparatus to permit the maintenance of a carbon dioxide-free atmosphere over the sodium hydroxide standard solution (**4.2**).

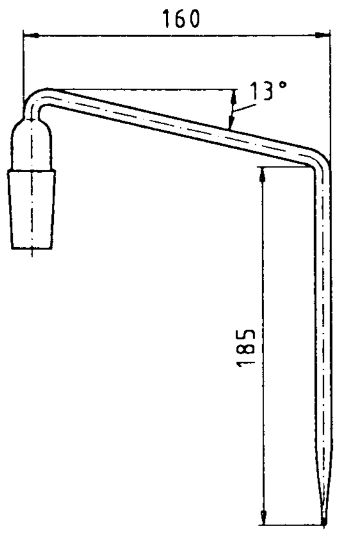
5.3 *Condenser coolant.*

Chill condenser with coolant, such as a circulating mixture of 1 part (volume fraction) of methanol and 2 parts of water, or continuous water flow, maintained at not more than 15 °C.

5.4 *Heating mantle*, capable of being controlled between 20 °C and 120 °C.

5.5 *Food processor* or *blender*.

5.6 *Oxygen absorber*, to guard against oxygen in nitrogen gas (**4.7**).



Dimensions in millimetres

Figure 2 — Enlarged diagram of bubbler for the distillation apparatus

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2) This description of a distillation apparatus refers to [1] in annex A and is given as information for the convenience of users of this European Standard. This information does not constitute an endorsement by CEN of the glassware named. Equivalent glassware (such as the distillation apparatus described in ISO 5522:1981, see [3] in annex A of this standard) may be used if it can be shown to lead to the same results.

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6 Procedure

6.1 General

Carry out sample preparation and analysis as quickly as possible to avoid loss of labile forms of sulfite.

NOTE To become familiar and proficient with the method before routine use, it is recommended that food test portions containing known amounts of sulfite are analysed. The analysis should be performed in a manner that precludes any loss of sulfite by oxidation or reaction with components in food. Since sulfites are reactive with air and food matrices and often lack stability, portions are fortified with a stable source of sulfite, not sodium sulfite or similar salts. Sodium hydroxymethylsulfonate (HMS), which is a bisulfite addition product of formaldehyde and which is structurally similar to some combined forms of sulfite in foods, is useful for preparing stable fortified test materials.

For analysis, 50 g of prepared sample of sulfite-free food are transferred to the flask (Figure 1; item 3). An aliquot portion of aqueous solution of HMS sodium salt is added. The solution is analysed immediately.

HMS recoveries of more than 80 % from food matrices fortified at 10 mg/kg are recommended to ensure accurate analytical data.

6.2 Sample preparation

6.2.1 *Solid samples*

Transfer 50 g of food, or a quantity that contains 500 µg to 1500 µg of sulfur dioxide, to a food processor or blender. Add 100 ml of the ethanol/water mixture (**4.6**) and briefly grind the mixture. Continue the grinding or blending only until the food is chopped into pieces small enough to pass through the ground glass joint of the flask (Figure 1; item 3).

6.2.2 *Liquid samples*

Mix 50 g of test sample, or quantity that contains 500 µg to 1500 µg of sulfur dioxide, with 100 ml of the ethanol/water mixture (**4.6**).

6.3 System preparation

Use the distillation apparatus (**5.1**) assembled as shown in Figure 1, put the flask (Figure 1; item 3) in the heating mantle (**5.4**) and add 400 ml of water to the flask. Close the stopcock of the funnel (Figure 1; item 2) and add 90 ml of hydrochloric acid solution (**4.1**) to the funnel. Begin nitrogen flow at 200 ml/min ± 10 ml/min and initiate the condenser coolant (**5.3**) flow. Add 30 ml of 3 % hydrogen peroxide solution (**4.4**) to the vessel (Figure 1; item 7). After 15 min, the apparatus and water will be thoroughly deoxygenated and the prepared test portion may be introduced into the apparatus.

6.4 Sample introduction and distillation

Remove the dropping funnel (Figure 1; item 2) and quantitatively transfer the test portion in aqueous ethanol to the flask (Figure 1; item 3). Wipe the tapered joint clean with a laboratory tissue, quickly apply stopcock grease to the outer joint of the funnel, and return the funnel to the flask. Examine each joint to be sure that it is sealed.

Use a rubber bulb equipped with a valve to apply head pressure above the hydrochloric acid solution in the funnel. Open the stopcock of the funnel and let hydrochloric acid solution flow into the flask. Continue to maintain sufficient pressure above the hydrochloric acid solution to force the solution into the flask. The stopcock may be closed, if necessary, to pump up pressure above the acid, and then opened again. Close the stopcock before the last 2 ml to 3 ml drain out of the funnel to guard against the escape of sulfur dioxide into the funnel.

Apply power to the heating mantle. Use a power setting that causes 80 drops/min to 90 drops/min of condensate to return to the flask from the condenser. Let the contents of the flask boil for 105 min, and then remove the vessel (Figure 1; item 7).

6.5 Determination and calculation

6.5.1 *Titration*

Immediately titrate (**5.2**) the contents of the vessel (Figure 1; item 7) with sodium hydroxide standard solution (**4.2**) to a yellow end point that persists longer than 20 s. Calculate the mass fraction, w, of sulfite, round the result without any decimal and express the sulfite content as sulfur dioxide in milligrams per kilogram, using equation (1).

$$w = \frac{32{,}03 \times V \times 1\,000 \times N}{m} \qquad (1)$$

where

32,03 is the milliequivalent weight of SO_2, in grams per mole;

N is the molarity of the sodium hydroxide standard solution, in mole per litre;

V is the volume of sodium hydroxide standard solution with $N = 0{,}010$ mol/l required to reach the end point in millilitres;

1 000 is the factor to convert milliequivalents to microequivalents;

m is the amount of test portion introduced into the round-bottomed flask (Figure 1; item 3), in grams.

6.5.2 *Blank determination*

Determine blank on reagents by titration and, if necessary, correct results accordingly.

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7 Precision

7.1 General

Details of the interlaboratory test according to ISO 5725:1986 (see [4] annex A) of the precision of the method are summarized in annex B. The values derived from the interlaboratory test may not be applicable to analyte concentration ranges and matrices other than given in the annex.

7.2 Repeatability

The absolute difference between two single test results found on identical test material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit, r, in not more than 5 % of the cases.

The values are:

Hominy	$\bar{x}$ = 9,2 mg/kg	r = 3,7 mg/kg
Fruit juice	$\bar{x}$ = 8,1 mg/l	r = 3,8 mg/l
Sea food	$\bar{x}$ = 10,4 mg/kg	r = 4,1 mg/kg

7.3 Reproducibility

The absolute difference between two single test results on identical test material reported by two laboratories will exceed the reproducibility limit, R, in not more than 5 % of the cases.

The values are:

Hominy	$\bar{x}$ = 9,2 mg/kg	R = 4,0 mg/kg
Fruit juice	$\bar{x}$ = 8,1 mg/l	R = 4,5 mg/l
Sea food	$\bar{x}$ = 10,4 mg/kg	R = 7,8 mg/kg

8 Test report

The test report shall contain at least the following:

— all information necessary for the identification of the sample;

— a reference to this European Standard or to the method used;

— the results and the units in which the results have been expressed;

— date and type of sampling procedure (if known);

— date of receipt;

— date of test;

— any particular points observed in the course of the test;

— any operations not specified in the method or regarded as optional which might have affected the results.

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Annex A (informative)

Bibliography

[1] Association of Official Analytical Chemists (AOAC International): Official Methods of Analysis (1995), 16th Edition, method 990.28, 47.3.43.

[2] Hillary et al: J. Assoc. Off. Anal. Chem. (Vol. 72, No. 3, 1989), p 470.

[3] ISO 5522:1981, *Fruits, vegetables and derived products — Determination of total sulfur dioxide content.*

[4] ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

Annex B (informative)

Precision data

In accordance with ISO 5725:1986 (see [4] of annex A), the following parameters have been identified in an interlaboratory test (see [2] of annex A). The test was conducted of the Food and Drug Administration (FDA).

Table B.1

Sample	Hominy	Fruit juice	Sea food
Year of interlaboratory test	1986	1986	1986
Number of laboratories	21	21	21
Number of samples	9	9	9
Number of laboratories retained after eliminating outliers	18	21	20
Number of outliers	3	0	1
Number of accepted results	39	42	41
Mean value ($\overline{x}$)	9,17 mg/kg	8,05 mg/l	10,41 mg/kg
Repeatability standard deviation (s_r)	1,33 mg/kg	1,36 mg/l	1,47 mg/kg
Repeatability relative standard deviation (RSD_r)	14,49 %	16,90 %	14,13 %
Repeatability limit (r)	3,72 mg/kg	3,81 mg/l	4,12 mg/kg
Reproducibility standard deviation (s_R)	1,42 mg/kg	1,62 mg/l	2,77 mg/kg
Reproducibility relative standard deviation (RSD_R)	15,50 %	20,14 %	26,62 %
Reproducibility limit (R)	3,98 mg/kg	4,54 mg/l	7,76 mg/kg

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